
LETTERS
TO THE EDITOR

Dedicated to the 115th anniversary of B.A. Arbuzov's birth

Phosphorylation of Betti Base with Bis(diethylamino)phosphoryl Chloride

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Abstract—The reaction of bis(diethylamino)phosphoryl chloride with *N*-Boc-protected 1-(α -aminobenzyl)-2-naphthol (Betti base) proceeded via *O*-phosphorylation of the phenolic OH group to form the target product as trifluoroacetate salt. The latter reacted with *O,O*-diethyl thiophosphoryl isothiocyanate to give thiourea bearing a chiral Betti base fragment.

Keywords: Betti base, phosphorylation, thiourea

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Chiral organophosphorus compounds are widely used in modern asymmetric synthesis both as organo-catalysts or chiral ligands, and as building blocks for the production of biologically active substances [1–5]. In this regard, the search for methods for synthesizing new specimens of this class of compounds is an urgent task.

In continuation of our work on the study of the possibility of phosphorylation of the Betti base and its derivatives [6–9] with the aim of further application in the asymmetric synthesis of phosphorus compounds, we chose bis(diethylamino)phosphoryl chloride as the phosphorylating agent. The introduction of additional active groups into the chiral Betti base molecule increases its functionality. In particular, the bis(diethylamino)phosphoryl group having pronounced basic properties can provide the molecule with additional activity when binding proton donors.

Direct phosphorylation of the Betti base is difficult due to the presence of two active nucleophilic proton-containing centers in the 1-(α -aminobenzyl)-2-naphthol molecule that can compete in reaction with electrophilic phosphorylating agents [7]. For selective

O-phosphorylation, we carried out preliminary Boc-protection of the amino group of the Betti base by reacting with di-*tert*-butyl dicarbonate (Scheme 1). As a result, the product **1** was obtained, which reacted with tetraethyl diamidochlorophosphate in the presence of potassium *tert*-butylate to form compound **2** ($\delta_P = 13.68$ ppm, Scheme 1). To remove the Boc-protecting group, compound **2** without isolation was treated with trifluoroacetic acid to form trifluoroacetate **3**.

It should be noted that the free base cannot be isolated from the salt with trifluoroacetic acid even when treated with an aqueous solution of sodium carbonate. In the IR spectrum of **3**, the absorption band at 1686 cm^{-1} characteristic of the trifluoroacetate anion and the broad band of the ammonium group at 2933 cm^{-1} are retained. The reason for the high stability of compound **3** with respect to an aqueous solution of sodium carbonate was made clear by studying its structure by X-ray diffraction method (Fig. 1). It can be seen from the obtained data that all three protons of the ammonium group form strong hydrogen bonds: two with trifluoroacetic acid anions, and the third with strongly basic phosphoryl oxygen of